

THE DISTRIBUTION OF SOLUTE PROCESSES ON AN ACID HILLSLOPE AND THE DELIVERY OF SOLUTES TO A STREAM: II. EXCHANGEABLE Al^{3+}

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ABSTRACT

In order to identify the distribution of aluminium (Al) within an acid hillslope and its release to a stream, the spatial distribution of acid ammonium oxalate extractable Al (Al_o) and exchangeable Al^{3+} have been investigated on a podzolized hillslope in Bicknoller Combe, Somerset, UK. The eluviated Al from topsoils is mainly deposited in the lower soil horizons forming podzolic B horizons, but some Al flows downslope carried by lateral throughflow. Al oxides may provide the main source of exchangeable Al^{3+} on the study slope due to high soil acidity. Examination of the spatial distribution of exchangeable Al^{3+} suggests that the slope hollow, where active convergent throughflow occurs, and the saturation wedge at the base of the slope are the main delivery routes of dissolved Al^{3+} to the stream. Divalent base cations (Ca^{2+} and Mg^{2+}), supplied from atmospheric input and organic decomposition and carried by throughflow, exchange Al^{3+} via cation exchange reactions under high water content. Laterally illuviated Al oxides in the lower hollow adjacent to the saturation wedge probably provide a pool for continuous delivery of Al either as soluble or complexed forms to the stream via the saturated wedge. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: exchangeable Al^{3+} ; Al oxides; podzolization; throughflow; saturated wedge; soil acidification; catena

INTRODUCTION

The increase of dissolved aluminium (Al) in soil solution and surface water is one of the most important applied issues for hydrochemical study at the catchment scale (Ball and Trudgill, 1995). Al in soils is mobilized from upper soil horizons (A and E horizons) as either complexed forms with organic materials (Al-chelates) or soluble inorganic Al–Si–Fe sols (proto-imogolite and allophane). A large fraction of the mobilized Al is precipitated within the lower soil horizons forming podzolic B horizons (Mokma and Buurman, 1982; Anderson *et al.*, 1982). Cronan and Schofield (1979) first hypothesized that anthropogenic mineral acids (mainly NO_3^- and SO_4^{2-}) from atmospheric deposition can remobilize Al previously precipitated within the soil during podzolization or held on soil exchange sites, this Al being transported through the soil to adjacent surface waters. Although it is difficult to assess the relative contribution of anthropogenic and natural processes to soil acidification (see Robarge and Johnson, 1992), the significant release of Al to surface water has been widely verified in many podzolized catchments in northern Europe and America (e.g. Johnson *et al.*, 1981; Driscoll *et al.*, 1985; Bishop *et al.*, 1990; Muscott *et al.*, 1993).

The main flowpaths for the release of dissolved Al into the stream are considered to be peat layers or topsoils, where hydraulic conductivity is higher than in lower mineral soils, and Bh horizons, which are partially cemented and so enhance production of lateral throughflow (Neal and Christophersen, 1989). H^+ and inorganic Al^{3+} in stream waters are frequently explained by mixing various proportions of soil solutions from different horizons, lumping complex flowpaths over slopes into homogeneous compartments thought to represent chemically and hydrologically distinct soil layers. With the increasing availability of catchment

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chemistry and soil data, however, uncertainty concerning such an assumption has emerged (Wheater and Beck, 1995). While the dissolution processes of Al into the soil solution and hydrological pathways for the sources of acidic episodes in stream water have been the main focus of acidification research, the spatial variability of hydrochemical processes and the delivery of mobile Al from slope soils to surface waters is still poorly understood and largely unexplored (Christophersen *et al.*, 1993; Wheater and Beck, 1995). One notable exception is the work of Mulder *et al.* (1991): in the Birkenes catchment in Norway, they show that soluble Al^{3+} formed in a podzolized area upslope moves downslope via throughflow, and is, in part, absorbed at lower slope positions by exchangeable reaction with peats; this Al^{3+} can be rapidly released to the stream during storm events.

During the course of research on soil–landform relationships on a three-dimensional hillslope in the Quantock Hills, Somerset, UK, distinctive patterns of Al distribution have been identified. While soil acidification and its influence on stream water chemistry have not been studied in detail, the spatial patterns of Al appear to be closely connected with the delivery of soluble Al from a highly acidified hillslope to the stream. The aims of this paper are: (1) to investigate the spatial distribution of Al oxides and exchangeable Al^{3+} on a podzolized hillslope; and (2) to examine their possible connection with the hydrochemical response of the stream.

STUDY AREA

The study area is a small hillslope at Bicknoller Combe on the Quantock Hills in Somerset, UK (Figure 1). The overall hillslope profile shows the progression: flat interfluve–convex slope–steep straight slope–(weak) concave foot slope. A hollow extends upslope from the base of the slope almost reaching the flat interfluve. There are two springs at the base of the hollow, forming a seepage zone. A detailed description of the study slope may be found in Burt and Park (1999).

The three-dimensional arrangement of the slope hollow and spurs controls the general slope hydrology (Anderson and Burt, 1978; Burt *et al.*, 1984). Soil water potentials measured at the base of the slope show that the small saturated wedge at the base of the hollow expands rapidly during rainfall. The depth of the saturated wedge is not greatly affected by the precipitation input, but is controlled largely by the convergence of throughflow into the lower hollow from the adjacent spurs and from the upper hollow. Similar processes of convergence in the upper hollow act to maintain wetter conditions for longer periods in the hollow at the expense of the spur zones. The preservation of wetter soil in the hollow may allow more rapid lateral transmission of soil water than on the spurs.

The two hydrological characteristics of the study slope—convergence of throughflow towards the hollow from the spurs, and the saturated wedges at the base of the slope—have been confirmed by soil morphological analysis (Park *et al.*, 1996). The spatial distribution of soil zones found in the study slope is presented in Figure 1. The convergence of throughflow towards the hollow is clearly indicated in the extension of stagnogley podzols down the hollow from the convex shoulder slope; in these soils intensive gleying features occur above or inside the podzolic B horizons. The presence of the saturated wedge at the base of the slope is confirmed by the spatial arrangement of the seepage soils and gleyic orthic brown soils in which the lower parts of soil profiles are saturated by the fluctuating water table. In an investigation of the spatial distribution of Fe oxides and hydroxides at different soil depths, Park and Burt (1999) show that the spatial distribution of soil zones on the study slope is correlated with the spatial distribution and intensity of throughflow. The intensity of lateral throughflow through loose A horizons is high in podzolized upslope areas, but gradually decreases towards the base of slope. Such spatial variation of throughflow is mainly controlled by the presence of relatively impermeable subsurface soil layers, such as indurated horizons and podzolic B horizons, and slope configuration. The dominance of throughflow clearly extends downslope along the hollow, as reflected in the downslope extension of the stagnogley podzols, but vertical percolation suddenly becomes dominant from the middle hollow where ‘lateral podzolic soils’ occur.

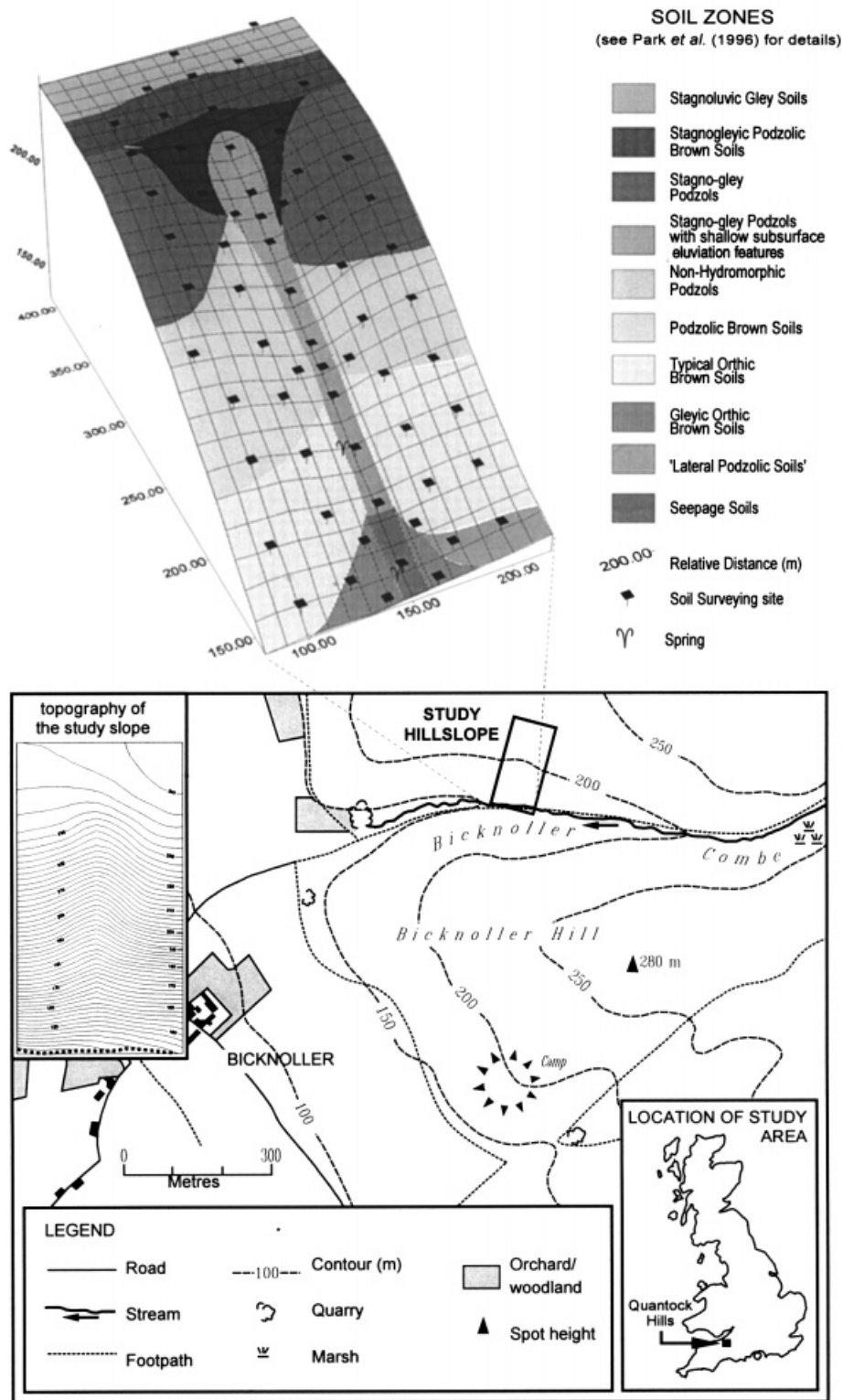


Figure 1. The location of the study site in Bicknoller Combe, the Quantock Hills, Somerset, and a podzolic catena development on the study slope.

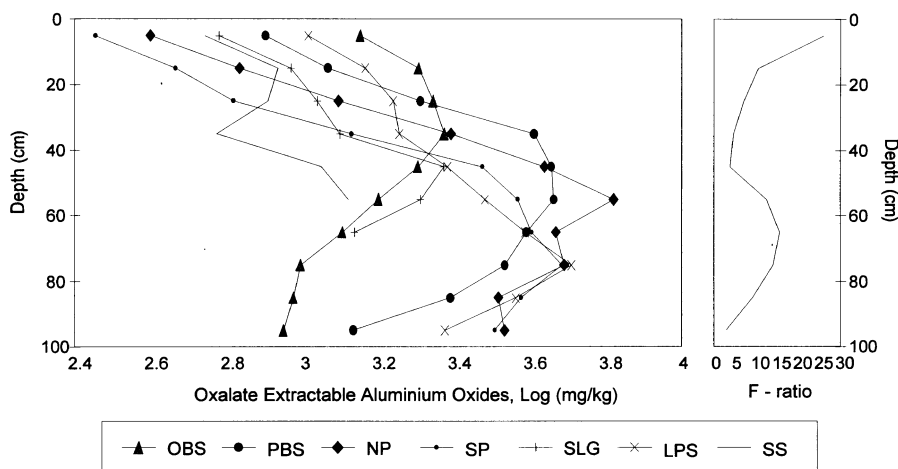


Figure 2. Vertical comparison of oxalate extractable Al oxides between seven different soil zones in Bicknoller Combe, Somerset. Total soil profiles ($n = 64$); OBS (orthic brown soils, $n = 14$); PBS (podzolic brown soils, $n = 13$); NP (non-hydromorphic podzols, $n = 12$); SP (stagnogley podzols, $n = 13$); SLG (stagnogley soils, $n = 8$); LPS ('lateral podzolic soils', $n = 5$); SS (seepage soils, $n = 2$)

METHODS

The same soil materials and statistical techniques of Burt and Park (1999) are used. Soil samples were collected from 64 soil profiles mainly based on a 25 m sampling grid (Figure 1). Pits varied in depth from 50 cm to 110 cm depending on the stoniness of the subsoil. Detailed soil descriptions may be found in Park *et al.* (1996). Exchangeable Al^{3+} was measured using an atomic absorption spectrophotometer after a single-step extraction with 0.1M $\text{BaCl}_2\text{--NH}_4\text{Cl}_2$ solution (Amacher *et al.*, 1990). Effective cation exchange capacity (ECEC) has been calculated in moles of charge of exchangeable cations ($\text{mmol}_c \text{ kg}^{-1}$) by the summation of seven extracted exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al^{3+} , Fe^{3+} and Mn^{2+}). In the calculation of ECEC, the extracted Al^{3+} is assumed to be the major component of exchangeable acidity (Amacher *et al.*, 1990). Since the vertical illuviation of Al oxides as imogolite and proto-imogolite allophane has been discovered in some podzolic soils in Scotland (Farmer *et al.*, 1983), acid ammonium oxalate extraction is considered the best extraction method for organic combined and amorphous Al in soils (Dahlgren, 1994). The extraction of Al oxides (Al_o) using acid ammonium oxalate follows the procedures of Ross and Wang (1993).

RESULTS

Spatial distribution of Al oxides

The level of Al_o is lowest in topsoil, increases rapidly to reach a maximum at 40–70 cm depth, and then decreases below that depth (Figure 2). This vertical pattern can be directly explained by the process of podzolization, which implies that a significant amount of Al is eluviated from topsoil in percolating water and illuviated in subsurface soils forming a podzolic B horizon. When the four soil zones developed across the slope are considered, it can be seen that the vertical distribution of Al_o reflects the intensity of podzolization well. This is assumed to increase in the following order: orthic brown soils < podzolic brown soils < non-hydromorphic podzols < stagnogley podzols. The Al_o content of topsoil decreases, and the depth of maximum illuviation generally increases with the increasing intensity of podzolization. A similar pattern is reported by Herbauts (1982). An exception to this pattern is the relatively low level of Al_o in the main podzolic horizons of stagnogley podzols.

Table I. F-ratio in the multiple comparison of exchangeable soil attributes between six soil zones in the study slope, the Quantock Hills, Somerset

Depth (cm)	F-ratio in ANOVA and probability							
	Oxalate extractable Al		CBD extractable Al		Exchangeable Al		Al saturation	
0–10 (<i>n</i> = 58) MC‡	25.90*	0.0000† 0↔1,2,3,4 1↔2,3/3↔4 5↔2,3	22.07	0.0000 0↔2,3,4 1↔3,4 3↔5	11.73	0.0000 0↔2,4/3↔4 1↔2,3,4	6.18	0.0001 1↔2 3↔0,1,4
20–30 (<i>n</i> = 64) MC	7.06	0.0000 3↔0,1	8.52	0.0000 3↔0,1,2 4↔0,1	6.45	0.0001 5↔0,1 0↔0,1	20.17	0.0000 5↔0,1,2,3,4 0↔1,2,3,4
40–50 (<i>n</i> = 64) MC	3.76	0.0049 0↔1,2	4.63	0.0012 0↔1,2 4↔1,2	16.27	0.0000 5↔1,2,3,4 0↔1,2,3,4	15.20	0.0000 5↔0,1,2,3,4 0↔1,2,3,4
60–70 (<i>n</i> = 59) MC	15.54	0.0000 0↔1,2,3,5 4↔1,2,3,5	17.71	0.0000 0↔1,2,3,5 4↔1,2,3,5	3.48	0.0081	12.96	0.0000 5↔1,2,3,4 0↔1,2,3,4
80–90 (<i>n</i> = 48) MC	9.13	0.0000 0↔1,2,3,5	8.61	0.0000 0↔1,2,3,5	2.10	0.0824	7.66	0.0000 5↔1,2,3 0↔1,3

* F-ratio of one-way ANOVA

† Probability of one-way ANOVA

‡ Multiple comparison of soil zones (Bonferroni test): 0, orthic brown soils; 1, podzolic brown soils; 2, non-hydromorphic podzols; 3, stagnogleyic podzols; 4, Stagnogleyic soils; 5, 'lateral podzolic soils' (see Figure 2 and Park *et al.* (1996) for details)

The F-ratio of Al_o in the upper 10 cm depth is relatively high (25.9), and individual soil zones are well differentiated by the Bonferroni test (Table I). In the map of Al_o for the upper soil layer (Figure 3A), the lowest Al_o levels occur on the eastern parts of the interfluvium, but the western parts of the interfluvium show relatively higher concentration. The eastern part of the interfluvium has a relatively high slope gradient; this declines towards the western parts of the interfluvium and the convex shoulder, providing better conditions for the leaching of Al. Along the main backslope, the lowest Al_o content occurs on the upper convex slope and extends downslope along the hollow. The level of Al_o gradually increases downslope along the spur and flank slopes. If a uniform distribution of Al oxides in parent materials across the slope is assumed, this spatial pattern may indicate the relative removal Al from topsoil by either vertical percolation or lateral throughflow.

The spatial distribution of Al_o becomes complicated in deeper soil layers, but some specific features can be recognized in Figure 3B–E. Firstly, there is a clear deficit of Al_o at 20–30 cm depth centred on the starting point of the hollow on the upper convex slope, and extending to the upper parts of the hollow. The low level of Al_o in the middle of the hollow is also observed at 40–50 cm. This low concentration of Al_o may be related to the high convergent throughflow within this slope segment. Secondly, high Al_o content occurs on the upper parts of the slope at 40–90 cm soil depth. This is apparently a result of the vertical illuviation of Al from topsoil during podzolization. On the other hand, there are low levels of Al_o on the lower parts of the slope, which can be easily explained by limited illuviation of Al in the orthic brown soils and water saturation in the seepage soils. One exception to this low content of Al_o downslope is the high level of Al_o in subsurface layers at the base of the upstream spur where 'lateral podzolic soils' occur. This spatial pattern is also recognized in the vertical comparison between soil zones (Figure 2). Al_o gradually increases from topsoil to the subsurface skeletal layer, while orthic brown soils, which are adjacent to the 'lateral podzolic soils', show significantly low levels in the deepest soil layers. Given the general occurrence of Al on the slope and limited podzolization in the topsoil of 'lateral podzolic soils', such an increase of Al_o seems to be a result of

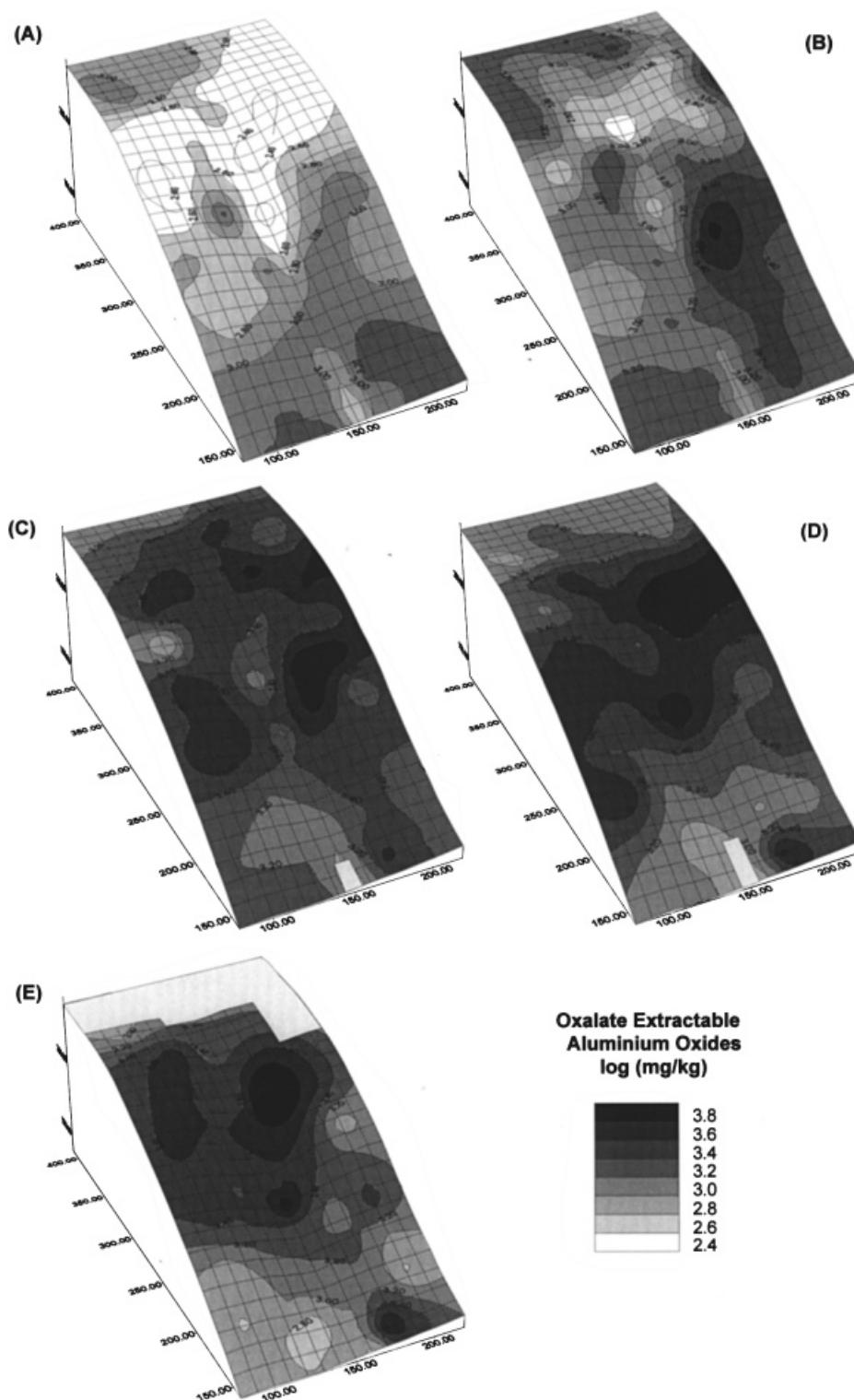


Figure 3. Spatial interpolation of oxalate extractable Al oxides in five soil layers in Bicknoller Combe, Somerset. (A) 0–10 cm depth ($n = 64$); (B) 20–30 cm depth ($n = 64$); (C) 40–50 cm depth ($n = 62$); (D) 60–70 cm depth ($n = 59$); (E) 80–90 cm depth ($n = 48$)

Table II. Regression equations for the exchangeable Al^{3+} (Ex. Al) with soil pH and Al oxides (Al_o) at different soil depths

Soil sample	Variables	r	R^2	F-ratio ($p < 0.001$)	Regression equation (Ex. Al =)
Total ($n = 502$)	Al_o	0.36**	0.162	96.75	$30.89 - 23.73 \text{ pH} + 8.43 \text{ Al}_\text{o}$
	pH	-0.40**	0.505	254.72	
0–10 cm ($n = 64$)	Al_o	0.71**	0.458	49.03	$6.45 + 13.16 \text{ Al}_\text{o} - 18.33 \text{ pH}$
	pH	-0.09	0.797	105.22	
20–30 cm ($n = 64$)	pH	-0.50**	0.247	21.69	$27.24 - 26.36 \text{ pH} + 11.40 \text{ Al}_\text{o}$
	Al_o	0.39**	0.632	55.87	
40–50 cm ($n = 62$)	pH	-0.80**	0.632	113.26	$71.59 - 37.65 \text{ pH} + 4.27 \text{ Al}_\text{o}$
	Al_o	0.26**	0.686	71.08	
60–70 cm ($n = 59$)	pH	-0.74**	0.538	71.09	$98.77 - 49.13 \text{ pH} + 2.49 \text{ Al}_\text{o}$
	Al_o	0.33**	0.579	38.55	
80–90 cm ($n = 48$)	pH	-0.70**	0.495	48.01	$94.06 - 48.15 \text{ pH} + 3.21 \text{ Al}_\text{o}$
	Al_o	0.31	0.585	33.76	

Stepwise variable selection: the soil variables are transformed with log transformation for Al_o and square root transformation for exchangeable Al and soil pH.

Significance level (two-tailed): * $p < 0.05$; ** $p < 0.01$

precipitation of Al brought into these soil layers by lateral throughflow from podzolized upslope areas (Park *et al.*, 1996).

One question raised by this explanation is why lateral illuviation of Al does not occur in the subsurface soil layers of 'lateral podzolic soils' in the hollow above the seepage soils (Figure 3). Park and Burt (1999) show strong lateral deposition of amorphous Fe inside the subsurface layers at this slope position, and argue that the illuviated Fe is mainly carried by convergent throughflow from podzolized soil upslope. When the general geochemical similarity between Al_o and Fe_o on the study slope ($r = 0.71$ – 0.88 , $p < 0.01$) and spatial arrangement of soil zones are considered, it is easy to conclude that significant amounts of Al will be carried into the subsurface skeletal layers combined with other soil colloids. The difference in pedological environments between the lower hollow and the base of the upstream spur is the intensity of convergent throughflow. While the lower hollow is frequently saturated by convergent flow due to the slope configuration, the base of the upstream spur experiences divergent flow (Anderson and Burt, 1978). This suggests that processes that may prevent illuviation of Al, or subsequently remove any illuviation products, are operating in the lower hollow.

Soil acidification

The average pH of the soils studied is 3.23 in 0.01 M CaCl_2 solution, ranging from 2.18 to 5.16. As indicated by the low soil pH, the soil exchangeable sites are dominated by Al^{3+} . The average cationic proportion of each exchangeable ion to ECEC is: Al^{3+} (79.60 per cent) > Ca^{2+} (9.98 per cent) > Mg^{2+} (4.12 per cent) > K^+ (3.78 per cent) > Na^+ (1.13 per cent) > Mn^{2+} (0.84 per cent) > Fe^{3+} (0.55 per cent). At this pH range ($\text{pH} < 4.5$), aluminosilicate clays and Al oxides begin to dissolve, releasing Al-hydroxy cations and Al^{3+} , replacing base cations from soil colloids (Bache, 1986). It may be concluded that exchangeable Al^{3+} is mainly generated from Al oxides under the high soil acidity of the study slope.

Exchangeable Al^{3+} is negatively correlated with soil pH, especially in the subsurface soil layers: no significant correlation exists for topsoil but there is a strong correlation ($r < -0.70$) for the deepest soil layers (> 40 cm depth) (Table II). The correlation between Al_o and exchangeable Al^{3+} shows the opposite trend: high positive correlation in topsoil ($r = 0.71$), but weaker with depth ($r \cong 0.3$). A multiple regression analysis shows that the variance of exchangeable Al^{3+} explained by soil pH and Al_o varies from 57 per cent to 79 per cent depending on the sampling depth (Table II). While the level of R^2 is low, one important generalization is evident from the regression equations. The relative contribution of soil pH to the explained variance of exchangeable Al^{3+} gradually increases with depth, but that of Al_o shows the opposite trend. These results may indicate that the amount of exchangeable Al^{3+} in topsoil is mainly controlled by the amount of Al oxide

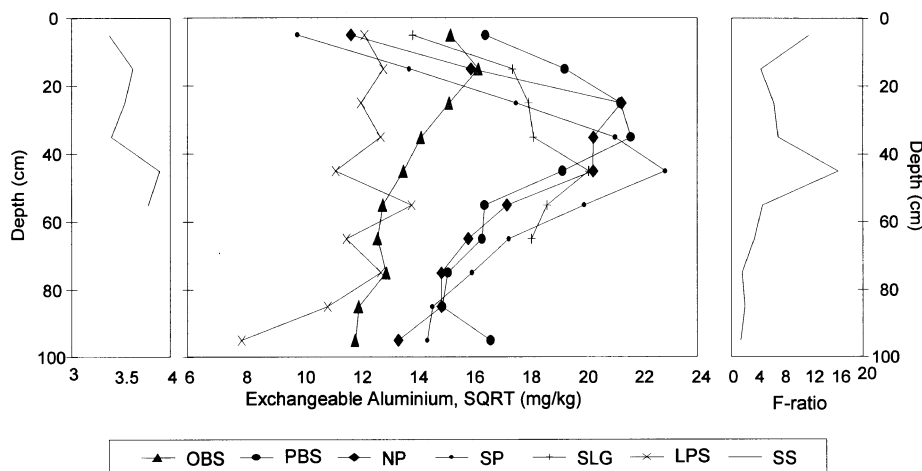


Figure 4. Vertical comparison of exchangeable aluminium between seven different soil zones in Bicknoller Combe, Somerset. Total soil profiles ($n = 64$); OBS (orthic brown soils, $n = 14$); PBS (podzolic brown soils, $n = 13$); NP (non-hydromorphic podzols, $n = 12$); SP (stagnogley podzols, $n = 13$); SLG (stagnogley soils, $n = 8$); LPS ('lateral podzolic soils', $n = 5$); SS (seepage soils, $n = 2$)

remaining in soils, because large amounts of Al oxides have already been removed from topsoil by percolation water and lateral throughflow. On the other hand, soil pH plays a more important role for the generation of exchangeable Al^{3+} in the subsurface soil layers where abundant Al oxides are available due to vertical illuviation.

Exchangeable Al^{3+} content is lowest in topsoil, increases to 40–50 cm depth, and decreases again below that depth (Figure 4). The vertical distribution of exchangeable Al^{3+} resembles that of Al_0 (Figure 2), even though the depth of maximum concentration is shallower than that of Al_0 in each soil zone. All podzolized soil zones shows a similar vertical distribution, but soil zones downslope show a different vertical distribution. The seepage soil zone shows an extremely low level of exchangeable Al^{3+} . The orthic brown soils and 'lateral podzolic soils' have lower levels of exchangeable Al^{3+} in subsurface soil layers than those of podzolized upslope soils.

Spatial distribution of exchangeable Al^{3+}

In topsoil, the lowest exchangeable Al^{3+} occurs in the lower hollow, and extends to the convex shoulder and upper backslope along the hollow (Figure 5A). The spatial distribution of low exchangeable Al^{3+} level closely matches the slope areas where active subsurface flow occurs, and where lateral throughflow is converging and flowing down to the stream (Park and Burt, 1999). The low exchangeable Al^{3+} content in the seepage zone has already been described in the vertical comparison between soil zones. As sampling depth increases, the low exchangeable Al^{3+} content in the lower hollow extends to the middle of the hollow, where the 'lateral podzolic soils' are located. This spatial pattern is clearly reflected in the fact that the 'lateral podzolic soils' have the lowest concentration of exchangeable Al^{3+} of any of the soil zones (Figure 4). The low level of exchangeable Al^{3+} extends from the lower hollow towards the lower spurs in the subsurface soil layers, where orthic brown soils and 'lateral podzolic soils' are located (Figure 5C–E).

By contrast, the high exchangeable Al^{3+} in upslope podzolic soils is clearly shown by the 20–30 cm and 40–50 cm maps (Figure 5B and C). On the 20–30 cm map, the highest level of exchangeable Al^{3+} occurs on the middle section of the hollow and spurs, and becomes more widespread on the upper parts of the slope including the interfluvium and upper convex slopes at 40–50 cm depth (Figure 5C). At 60–70 cm and more particularly at 80–90 cm (Figure 5E), the high levels of exchangeable Al^{3+} disappear, remaining relatively high only in the middle hollow, juxtaposed with the very low concentrations in the lower hollow. This spatial

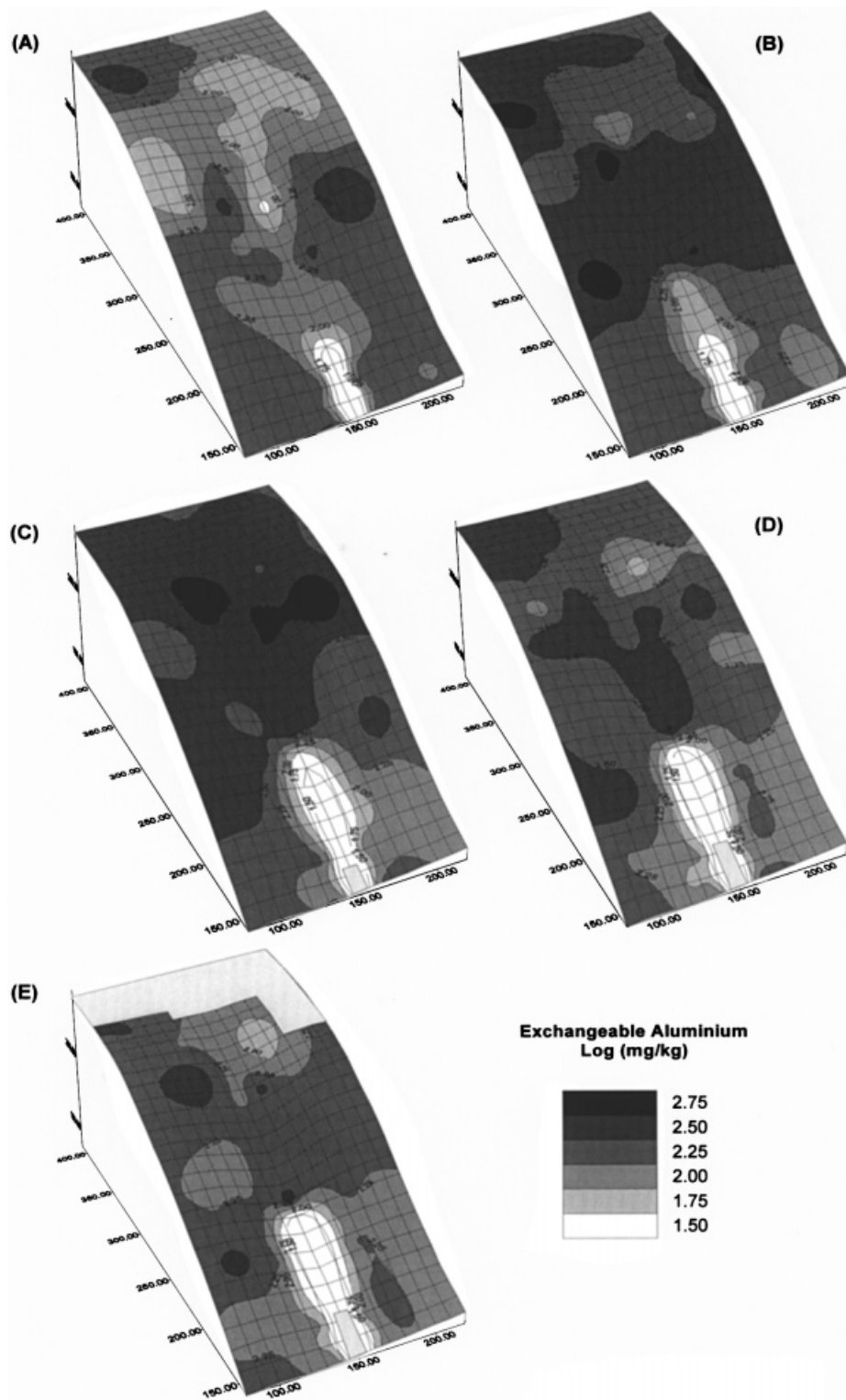


Figure 5. Spatial interpolation of exchangeable aluminium in five soil layers in Bicknoller Combe, Somerset. (A) 0–10 cm depth ($n = 64$); (B) 20–30 cm depth ($n = 64$); (C) 40–50 cm depth ($n = 62$); (D) 60–70 cm depth ($n = 59$); (E) 80–90 cm depth ($n = 48$)

Table III. Correlation matrix for compositional data of exchangeable cations in Bicknoller Combe, Somerset

	pH	LOI	Clay	ECEC	% Ca	% Mg	% Ca+Mg	% K	% Na	% Al	Al _o
pH	1	-0.39**	-0.00	-0.21**	0.22**	0.29**	0.25**	-0.25**	0.17**	-0.17**	0.42**
LOI	-0.39**	1	0.37**	0.55**	0.13**	0.08	0.11*	0.25**	-0.02	-0.14**	0.19**
Clay	-0.00	0.37**	1	0.45**	0.18**	0.15**	0.17**	0.15**	-0.07	-0.19**	0.18**
ECEC	-0.21**	0.55**	0.45**	1	-0.04	0.06	-0.01	-0.25**	-0.59**	0.09*	0.13**
% Ca	0.22**	0.13**	0.18**	-0.04	1	0.92**	0.99**	0.51**	0.53**	-0.98**	-0.40**
% Mg	0.29**	0.08	0.15**	0.06	0.92**	1	0.96**	0.42**	0.40**	-0.92**	-0.43**
% Ca+Mg	0.25**	0.11*	0.17**	-0.01	0.99**	0.96**	1	0.49**	0.49**	-0.98**	-0.42**
% K	-0.25**	0.25**	0.15**	-0.25**	0.52**	0.42**	0.49**	1	0.46**	-0.64**	-0.39**
% Na	0.17**	-0.02	-0.07	-0.59**	0.53**	0.40**	0.49**	0.46**	1	-0.57**	-0.14**
% Al	-0.17**	-0.14**	-0.19**	0.09*	-0.98**	-0.92**	-0.98**	-0.64**	-0.57**	1	0.44**
Al _o	0.42**	0.19**	0.18**	0.13**	-0.40**	-0.43**	-0.42**	-0.39**	-0.14**	0.44**	1

LOI, loss-on-ignition; ECEC, effective cation exchange capacity

Significance level (two-tailed): * $p < 0.05$; ** $p < 0.01$

Percentage values represent compositional percentage of each exchangeable cation to ECEC in mmol_c kg⁻¹.

arrangement suggests the possibility that exchangeable Al³⁺ can easily be leached by rapid subsurface throughflow from the podzolic horizons in upslope soils to the stream via the lower hollow.

Characteristics of soil exchangeable systems

The soil acidification and leaching processes of Al³⁺ are largely governed by cation exchange reactions in the soil (Bache, 1986; Robarge and Johnson, 1992). In a correlation matrix of cationic composition of each cation to ECEC (Table III), only exchangeable Al³⁺ has a negative correlation with other exchangeable cations. Considering that each individual cation competes for a given exchange site, this suggests that exchangeable Al³⁺ can replace other cations via cation exchange reactions. The correlation between the cationic fraction of exchangeable Al³⁺ (Al saturation; AS) and the fraction of divalent cations (Ca²⁺ and Mg²⁺ saturation; CMS) is particularly high: -0.98 with calcium, -0.92 with magnesium, and -0.98 with CMS. No such high association is found either with other exchangeable cations or with other physico-chemical soil attributes. AS and CMS show independent associations with clay and organic content, which provide the main cation exchange sites. These indicate that there are strong stoichiometric relationships between exchangeable Al³⁺ and exchangeable divalent cations for given exchangeable sites on the study slope. Because Al³⁺, Ca²⁺ and Mg²⁺ account for 93.7 per cent of ECEC, the spatial distributions of AS and CMS effectively summarize the general cation exchange reactions on the study slope.

AS is lowest in topsoil and rapidly increases to 30 cm depth (Figure 6); however, there is little difference in the level of AS below this depth. Because of their high association ($r = -0.98$), CMS shows an exactly opposite pattern to AS. The low AS and high CMS of upper soil layers, notwithstanding the fact that the lowest soil pH is at these soil depths, indicates that divalent cations occupy the soil exchangeable sites. This pattern is probably caused by the continuous supply of divalent cations from plant litter and atmospheric deposition (Burt and Park, 1999), while Al³⁺ is mainly derived from soil minerals, but large amounts of Al oxides have already been removed from topsoil by lateral throughflow and vertical illuviation. On the other hand, the subsurface soil layers below 30 cm depth, which are beyond the direct supply of divalent cations from atmospheric deposition and the decomposition of organic materials, have high Al levels due to strong soil acidity and high levels of illuviated Al oxides.

In a comparison of AS between each soil zone, the seepage soil is unique, having an extremely low AS (Figure 6). Most exchange sites in the seepage soils are occupied by Ca²⁺ and Mg²⁺. This soil zone undergoes frequent saturation by shallow ground water. Burt and Park (1999) show that Ca²⁺, Mg²⁺ and Na⁺, carried by convergent throughflow, are absorbed on exchange sites in the lower hollow and within the saturated wedge. A similar increase in Ca²⁺, Mg²⁺ and Na⁺ on exchange sites is also observed in the water-

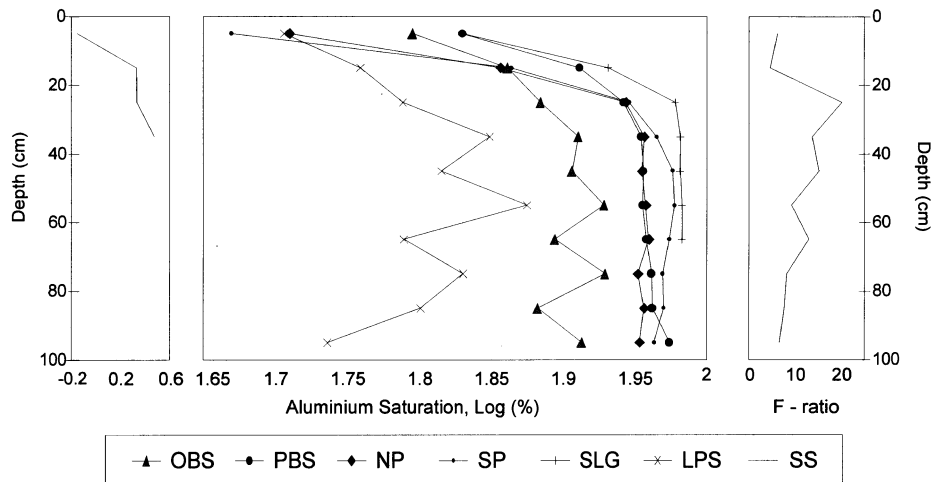


Figure 6. Vertical comparison of aluminium saturation between seven different soil zones in Bicknoller Combe, Somerset. Total soil profiles ($n = 64$); OBS (orthic brown soils, $n = 14$); PBS (podzolic brown soils, $n = 13$); NP (non-hydromorphic podzols, $n = 12$); SP (stagnogley podzols, $n = 13$); SLG (stagnogley soils, $n = 8$); LPS ('lateral podzolic soils', $n = 5$); SS (seepage soils, $n = 2$)

saturated parts of 'lateral podzolic soils' and orthic brown soils, where low exchangeable Al^{3+} and AS occur (Figure 6). One complicating factor, however, is that a low level of exchangeable Al^{3+} is associated with less advanced soil acidification in these two soil zones. These two soil zones show relatively high soil pH, which implies that exchangeable Al^{3+} occupies fewer of the exchange sites. Exchangeable Al^{3+} in these two soil zones drops below the 20–30 cm depth (Figure 4). Hence, it is hard to argue that water saturation, leading to a high level of base cations at the base of these soil profiles, is solely responsible for the decrease in exchangeable Al^{3+} .

One clear feature in the first AS map (Figure 7A) is the area of low AS starting from the upper convex slope–interfluvium and extending downslope along the hollow. This pattern is absent for the subsoil layers (Figure 7B–E); instead there is a clear separation between the high AS area upslope and the low AS area in the lower hollow and spurs. A clear zone of low Al saturation, extending from the middle hollow to the stream and gradually extending towards the downstream spur and also to the upstream spur in deeper soil layers, can be recognized on the 60–70 cm and 80–90 cm maps. It must be noted that the zones of low AS accord with areas where high subsurface flow occurs, as established by soil water potential measurement (Anderson and Burt, 1978; Burt *et al.*, 1984), and soil morphological analysis (Park *et al.*, 1996).

DISCUSSION: POSSIBLE MECHANISMS FOR Al DELIVERY FROM SLOPE SOILS TO THE STREAM

While soil acidification and its influence on stream water chemistry has not been explicitly studied during this research, it is to be expected that there is active Al^{3+} leaching from such a highly acidified slope to the stream. The exchangeable Al^{3+} in acid soils provides a large reserve of adsorbed ionic Al^{3+} that can be rapidly mobilized into solution, whilst the dissolution of Al oxides from any primary aluminosilicate minerals may also play a major role in the buffering of mineral soil solution acidity (Bache, 1986; McBride, 1994).

During the investigation of exchangeable Al^{3+} , some important spatial patterns have been recognized; these may be closely related to ionic Al^{3+} delivery from slope soils to the stream.

- (1) Clear depletion of exchangeable Al^{3+} occurs on the upper slope and extends to the base of the slope along the hollow. This area of Al depletion closely matches the area where a large amount of lateral throughflow

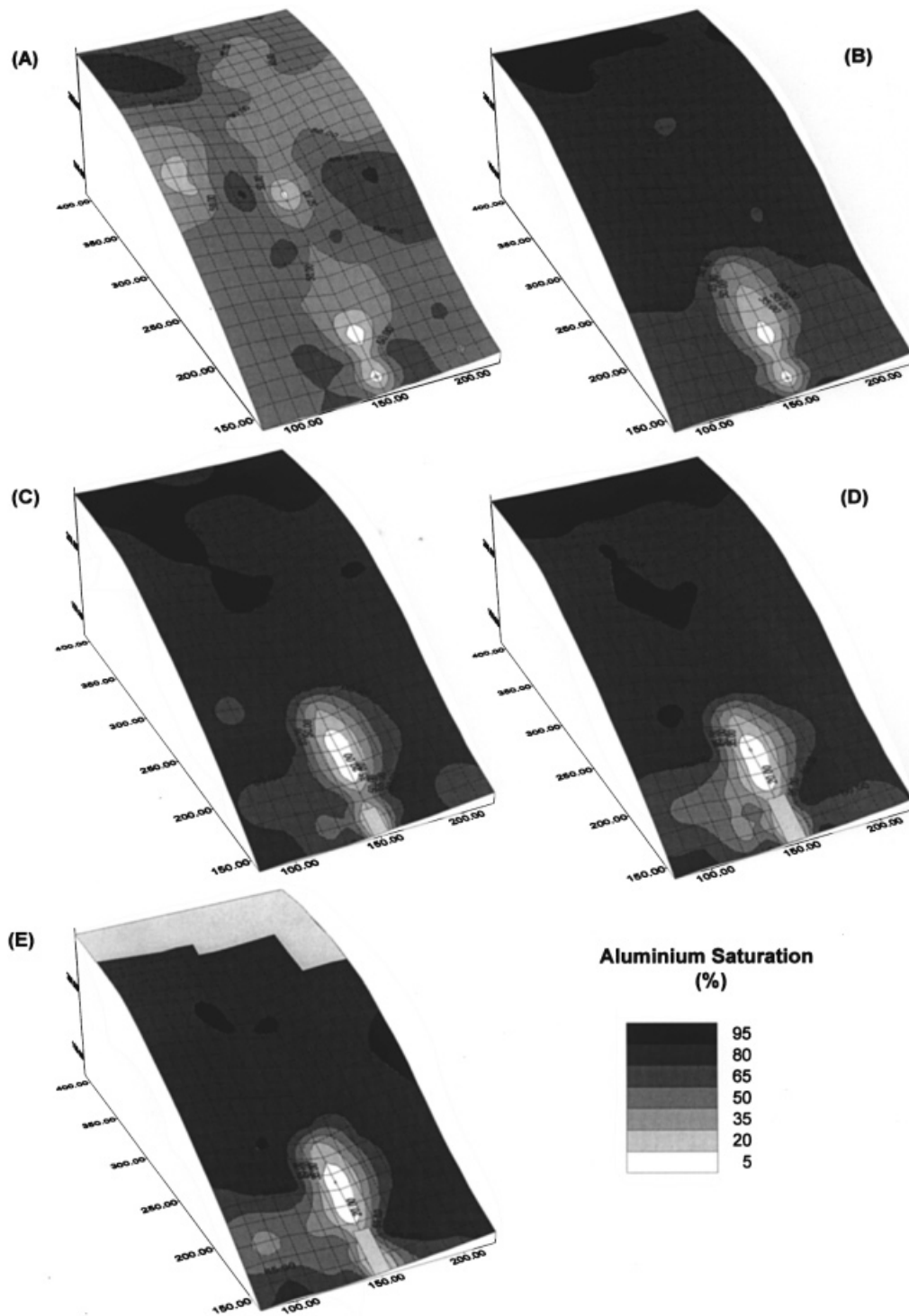


Figure 7. Spatial interpolation of aluminium saturation in five soil layers in Bicknoller Combe, Somerset. (A) 0–10 cm depth ($n = 64$); (B) 20–30 cm depth ($n = 64$); (C) 40–50 cm depth ($n = 62$); (D) 60–70 cm depth ($n = 59$); (E) 80–90 cm depth ($n = 48$)

occurs. This spatial distribution is quite unlike the homogeneous spatial distribution of divalent exchangeable cations in the topsoil (Burt and Park, 1999).

- (2) The lower hollow, where abundant convergent subsurface flow and a saturated wedge occur, shows remarkable depletion of exchangeable Al^{3+} associated with an increase in exchangeable Ca^{2+} and Mg^{2+} . The depletion zone is directly connected to the high level of exchangeable Al^{3+} in the subsurface illuvial horizons of upslope podzolic soils.
- (3) The depletion of exchangeable Al^{3+} expands with depth towards the spurs at the base of the hillslope, where the saturated wedge also expands during wet periods. These observations lead to the conclusion that there is depletion of exchangeable Al^{3+} from the soils and slope areas where high water contents occur, and that Al-depleted soil exchange sites are mainly occupied by divalent cations.

These spatial patterns may be explained by cation exchange reactions, in which divalent cations (Ca^{2+} and Mg^{2+}) in incoming soil waters replace Al^{3+} from soil exchange sites. In most acid soil mineral horizons, Ca^{2+} , Mg^{2+} and Al^{3+} are the dominant ions at the exchange surface, and Ca^{2+} – Mg^{2+} and Al^{3+} compete for given soil exchange sites. This is confirmed in the study soils (Table III). A sudden increase in levels of soluble Al^{3+} with H^+ in drainage water and soil solution soon after an increase in the concentration of Ca^{2+} (and other base cations) is a well-established phenomenon in laboratory and catchment experiments (Wiklander, 1975; Reuss, 1983; Wright *et al.*, 1988). It is widely known as the 'sea-salt effect' in coastal regions, where episodic inputs to acid soils of precipitation rich in sea salt can cause acidification of runoff. The main mechanism for this phenomenon involves a fraction of the incoming base cations in sea salt being exchanged for other cations, notably Al^{3+} , in the acidified soils (Wright *et al.*, 1988).

Similar processes presumably occur on the study slope due to the extremely acid soils and proximity to the sea. Monitoring of Al^{3+} in the stream water was beyond the scope of this research, and there is only a little information available concerning Al^{3+} concentrations in the stream. In his description of the variation of solute concentrations in stream water, Burt (1978, p.468) briefly mentioned that Al^{3+} concentration may have approached Mg^{2+} concentrations ($2\text{--}4\text{ mg l}^{-1}$) during storm discharge peaks in the local stream. This observation raises the possibility of a 'sea-salt effect' at the study site.

It is reasonable to treat the depletion of exchangeable Al^{3+} in topsoil and subsurface soils separately, because of the difference in slope hydrological processes with depth and the influence of vegetation. In topsoil, divalent cations are closely held in the study slope under the soil–vegetation system, continuously supplied by atmospheric input and by nutrient cycling following decomposition of organic materials (Burt and Park, 1999). During rainfall, divalent cations supplied from the decomposition of organic materials and deposition by rainwater may flow both downprofile (under the influence of infiltration) and downslope (according to hillslope configuration). On the way downslope, the concentration of divalent cations in throughflow gradually increases, and divalent cations may then replace Al^{3+} from exchangeable sites despite the high soil acidity in the topsoil, which results in the depletion of Al^{3+} from soil exchange sites. Owing to the high intensity of podzolization and consequent depletion of Al oxides in topsoil, this process is rather slow to release soluble Al^{3+} to the stream, especially when compared with processes occurring in the lower hollow.

A similar mechanism may also be at work in the depletion of Al^{3+} in the lower hollow and the saturated wedge. Unlike Al^{3+} , which is subject to deposition when it meets less acidic subsurface soils, divalent cations flow downslope according to the hydraulic gradient. As time passes, the concentration of divalent cations in throughflow water gradually increases due to evapotranspiration and the longer contact time between soil water and minerals. Therefore it is to be expected that water reaching the lower hollow has a higher concentration of divalent cations. This results in an increase of Ca^{2+} , Mg^{2+} and Na^+ in the water-saturated parts of the lower slope hollow (Burt and Park, 1999). The divalent cations in convergent throughflow may displace Al^{3+} from soil exchange sites. Compared with processes operating in topsoil, this process is thought to be quite active in the release of Al^{3+} to the stream. As observed in Figure 6, the zone with the highest levels of exchangeable Al^{3+} in the subsurface soils of the podzolized upper slope lies very close to the Al-depleted zone in the middle hollow.

The low level of Al_o in the lower hollow may also be related to active removal of Al from this part of the hillslope (Figure 4). A significant amount of Al may be carried laterally into the subsurface skeletal layers of 'lateral podzolic soils', combined with other soil colloids (Park and Burt, 1999). It is not clear whether the absence of illuviation of Al in these soils is caused by direct removal of mobilized Al oxides to the stream or by *a posteriori* dissolution processes of illuviated oxides. If it is assumed that precipitation of Al oxides occurs first, the illuviated Al oxides from upslope may be easily dissolved by the strong acidity and convergent throughflow in this slope position. Because amorphous Al oxides are those most easily dissolved Al^{3+} reservoirs in soils (Bache, 1986), illuviated Al oxides may be acting as a pool for the continuous release of Al^{3+} to the stream. On the other hand, the direct removal of Al oxides to the stream is also possible. In the comparison of Al_o and CBD extractable Al (Al_d), the Al_o/Al_d ratio frequently exceeds one in the subsurface layers of the 'lateral podzolic soils', which indicates the presence of soluble inorganic Al–Si–Fe sols in the lower parts of the hollow (Park, 1997). In order to understand the removal characteristics of Al oxides from this slope area, further study would be necessary along with a more accurate mineralogical identification of individual Al oxides.

CONCLUSION

This research has described the spatial distribution of Al on an acid hillslope and inferred the possible spatial connection between Al storage in slope soils and the hydrochemical response of the stream. The spatial distribution of Al is largely governed by the intensity of podzolization, which in turn is determined by subsurface water flow both vertically and laterally (downslope). The Al oxides eluviated from topsoil by percolation are mainly precipitated in the lower soil layers forming podzolic B horizons. While accurate quantification has not been achieved in this research, eluviated Al seems to move downslope in throughflow, some Al being directly released into the stream, while the rest is probably precipitated in the subsurface layers of soils on the lower slope. Al oxides may provide the basic source of exchangeable Al^{3+} because of the high soil acidity and the low level of primary minerals in the parent material.

During this examination of the spatial distribution of exchangeable Al^{3+} , two main delivery routes of Al^{3+} from slope soils to the stream have been proposed on the study slope. The first is the main part of the slope hollow where convergent throughflow occurs, mainly during storm events, and the second is the saturated wedge present in the lower hollow, where convergent throughflow and return flow occur. The fundamental process involved is the replacement of Al^{3+} by divalent base cations (Ca^{2+} and Mg^{2+}), which are supplied from atmospheric deposition and organic decomposition, via cation exchange reactions in a water-saturated environment. The release of Al^{3+} is more active in the saturated wedge and the lower hollow, because of the close spatial connection with high level of Al oxides and exchangeable Al^{3+} .

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